

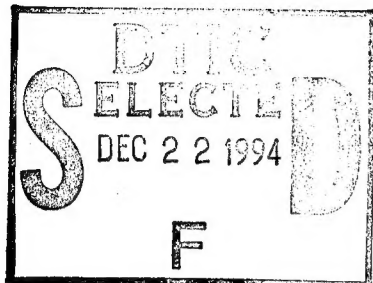
OFFICE OF NAVAL RESEARCH

GRANT N00014-93-1-0534

R&T Code 413x004

Program Manager Dr. K. Wynne

Technical Report No. 1



Materials with Self Organized Surfaces:
2D Polymer Assemblies

by

Samuel I. Stupp, Vassou Le Bonheur, and Kenneth A. Walker

Submitted for presentation at the American Chemical Society meeting

in Anaheim, CA

April 2-7, 1995

Department of Materials Science and Engineering
University of Illinois
Urbana, IL 61801

December 1, 1994

Reproduction in whole or in part is permitted for any purpose of the United States
Government

This document has been approved for public release and sale;
its distribution is unlimited.

19941216 079

DTIC QUALITY INSPECTED 1

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

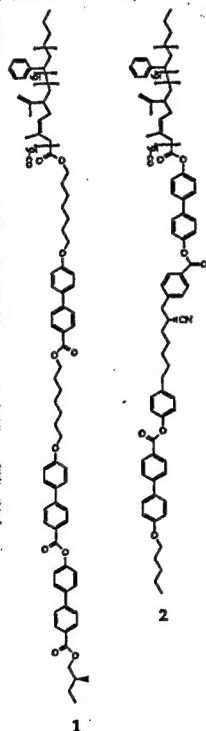
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE December 1, 1994		3. REPORT TYPE AND DATES COVERED Technical 5/1/93 - 4/30/94	
4. TITLE AND SUBTITLE Materials with Self Organized Surfaces: 2D Polymer Assemblies				5. FUNDING NUMBERS N00014-93-1-0534 R&T Code: 413x004 Dr. Kenneth J. Wynne	
6. AUTHOR(S) Samuel I. Stupp, Vassou Le Bonheur, and Kenneth A. Walker					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Departments of Materials Science and Engineering University of Illinois 1304 W. Green St, Urbana, IL 61801				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Kenneth J. Wynne Office of Naval Research Department of the Navy 800 North Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Submitted for presentation at the American Chemical Society Meeting in Anaheim, CA, April 2-7, 1995					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government; this document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Our laboratory has developed the concept of "bulk" synthesized 2D polymers through self assembly of reactive oligomers into layered structures. The products from these supermolecular reaction schemes are high molar mass flat macromolecules which in fusible systems retain their shape during solid to liquid phase transitions. We describe here a new system based on nanophase separated rodcoils functionalized at one terminus with the objective of producing 2D polymers with two chemically different surfaces. One surface of the macromolecule contains closely packed methyl groups and it is therefore highly hydrophobic, whereas the other is hydrophilic being composed of phenolic or carboxyl functions. Interestingly, solvent cast "macroscopic" films of the layered assemblies develop spontaneously one hydrophobic surface and a very sticky one which is readily wet by water. This observation is possibly the first example of a bulk material with self organized surfaces, an important objective for the exploitation of self assembly in manufacturing. Such materials would open the door to concepts such as self organized interfaces for composite materials, self organized tapes and membranes with chemically defined surfaces, as well as tubes with chemically defined lumina.					
14. SUBJECT TERMS 2D polymer, contact angle, hydrophobic surface, hydrophilic surface				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL		

Materials with Self Organized Surfaces:
2D Polymer Assemblies

S.I. Stupp, V. LeBonheur, and K. Walker, Departments of Materials Science and Engineering and Chemistry, Beckman Institute for Advanced Science and Technology, and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Over the past few years our laboratory has developed the concept of "bulk" synthesized 2D polymers which derive from the self assembly of reactive oligomers into layered structures (1,2). We have four distinct methodologies in place, molecular recognition among chiral oligomers, nanophase separation of rodcoil block structures, self assembly of molecules into layered hairpins, and the very recently developed approach involving hydrogen bonding among comb polymers. The products from these super-molecular reaction schemes are high molar mass flat macromolecules which in fusible systems retain their shape during solid to liquid phase transitions. In the first system developed (1), 2D polymers were formed which can stack at room temperature into single crystal assemblies and upon melting retain their flat molecular architecture as demonstrated by the smectic nature of their fluid state.

The second generation of precursors were rodcoil structures (2) which self assemble into layers containing three sub-layers, each a few nanometers in thickness. The general tendency of rodcoil structures to nanophase separate is clearly established in a recent publication from our group using molecules which are of much higher molecular weight than those used to synthesize 2D polymers (3). A typical construction contains a protecting sub-layer, a reactive sub-layer in which crosslinking occurs within a 2D space confined by the protecting sub-layer, and a third rigid sub-layer functions as the shape-granting skeleton of the molecular object. Typical rodcoil structures synthesized in our laboratory are shown below,



The work described here focuses on the surface properties of rodcoil-derived 2D polymers. We prepared solution cast films of 2D polymer from rodcoil precursor 1 and measured the contact angle of water on their surfaces. As a control we prepared Langmuir-Blodgett films using a similar rodcoil and also measured contact angles. We found that both the solution cast film and the LB film have identical contact angles in both value and uniformity. Furthermore we were able to change the stacking direction of 2D polymers on solution cast films depending on the substrate used. These results are summarized schematically in figure 1.

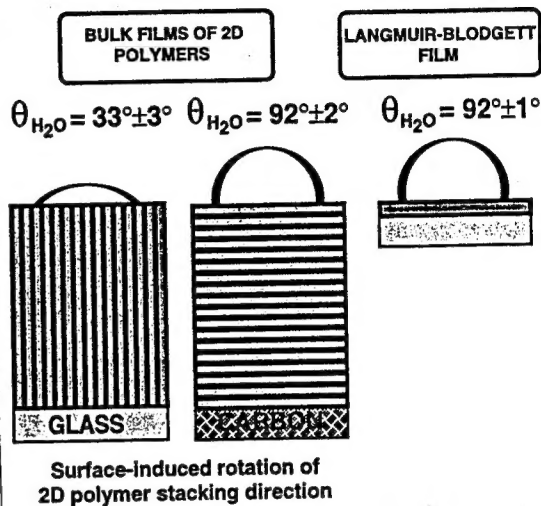
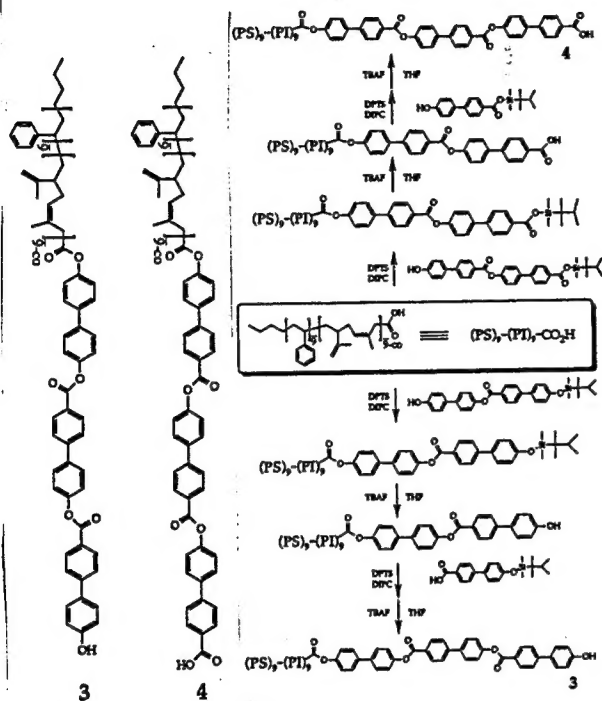


Figure 1

The results obtained on surface properties of solvent cast films suggest the concept of materials with self-organized surfaces. Macroscopic stacking of these 2D assemblies with a single stacking direction would generate films with surfaces having the same chemical structure present on the surfaces of the 2D molecular objects.

We introduce here rodcoil structures 3 and 4 functionalized at one terminus with the objective of producing 2D polymers with two chemically different surfaces. One surface of planar macromolecules prepared with these precursors would contain closely packed methyl groups and would therefore be highly hydrophobic, whereas the other one would be hydrophilic being composed of phenolic or carboxyl functions. These rodcoils are synthesized using the following scheme,



Both rodcoil molecules exhibit smectic phases and reveal exotherms in differential calorimetry scans fingerprinting the crosslinking reaction necessary to form 2D polymers. Most importantly, following the reaction the product obtained flows as a birefringent melt with extremely high thermal stability. This clearly indicates the product is not a crosslinked network but ensembles of planar molecular objects.

We have studied so far the surface properties of 5 and found that solvent cast "macroscopic" films of these molecules develop spontaneously one hydrophobic surface and a very sticky one which is readily wet by water. Shown below is a schematic representation of the film's ideal molecular structure and of the results obtained on its surface properties.

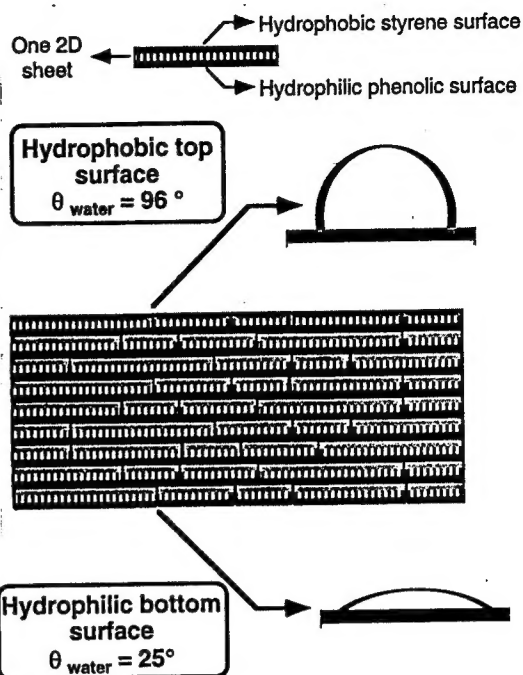


Figure 2

This observation is possibly the first example of a bulk material with self organized surfaces, an important objective for the exploitation of self assembly in manufacturing. Such materials would open the door to concepts such as self organized interfaces for composite materials, self organized tapes and membranes with chemically defined surfaces, as well as tubes with chemically defined lumina.

ACKNOWLEDGEMENTS

The authors are grateful to the Office of Naval Research, Chemistry Division for support of this work through grant N00014-93-1-0534.

REFERENCES

- 1) S. I. Stupp, S. Son, H. C. Lin, and L. S. Li, *Science*, **259**, 59, (1993).
- 2) S. I. Stupp, M. S. Lee, S. Son, L. S. Li, and M. Keser, *ACS Polymer Preprints*, **34**, (1), 184, (1993).
- 3) L. H. Radzilowski and S. I. Stupp, *Macromolecules*, in press.

Accession For	
NTIS CRA&I	
DTIC TAB	
Unannounced	
Justification	
By	
Date	
A-1	